Melt Viscosity of Main-Chain Thermotropic Liquid Crystalline Polymers without Flexible Spacers

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ABSTRACT: Viscoelastic properties for a series of all-aromatic main-chain thermotropic copolymers based on random units of 75% 1-hydroxy-4-benzoic acid and 25% 2-hydroxy-6-naphthoic acid (B–N, 3:1) were measured in the nematic state. Zero-shear rate viscosity η_0 obtained from small-strain oscillatory and steady-state measurements reveals that η_0 scales with the molecular weight with a power of 4.1, i.e., $\eta_0 \propto M^{4.1}$. Measurements of viscosity for the small-molecule liquid crystal (SMLC) bis[4-(phenoxycarbonyl)-phenyl] 1,4-benzenedicarboxylic acid ester and data for other SMLC compounds taken from the literature establish that this power dependence holds over a range covering 3 decades in molecular weight and 8 decades in viscosity. This exponent 4.1 is distinctly different from that of conventional polymer melts, 3.4, but lies within the range of values reported for nematic polymers with flexible spacers.

Introduction

Liquid crystalline polymers (LCPs) are of interest, not only because of their use in specialty moldings and films but also because understanding them presents a particular scientific challenge.[1,2] The mesogenic units which generate the liquid crystalline phase can either form an integral part of the chain backbone (main-chain LCPs) or be attached to it (side-chain LCPs). This work deals only with main-chain LCPs. The shear flow behavior of small-molecule liquid crystals (SMLC) is well understood in its fundamentals, being described by the Leslie–Ericksen–Parodi theory [3]. Simultaneously, molecular models and continuum theories which describe the flow behavior of conventional flexible polymers have been developed over the years, and linear and nonlinear viscoelastic response either in solution or in bulk is quite well understood.[4]

However, it is not clear that the melt flow behavior of LCPs resembles either that of small-molecule nematics or that of ordinary polymers. The flow phenomena cannot be explained by any of the accepted theories nor by a trivial combination of them. The establishment of the experimental dependence of the flow properties, and in particular the zero-shear viscosity η_0, on molecular weight is an important step in understanding the rheology of LCPs.

We report here on viscosity measurements for wholly aromatic main-chain thermotropic copolyesters in the nematic phase.[5] They are complemented by measurements on a symmetric aromatic ester oligomer and are compared with viscosity values reported in the literature for other SMLCs and for main-chain LCPs with flexible spacers in the backbone. A power dependence covering 3 decades in molecular weight and 8 decades in viscosity is obtained.

Experimental Section

Measurements were made on a molecular weight series of main-chain thermotropic liquid crystalline polymers based on random units of 1-hydroxy-4-benzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) in the ratio of 75:25, designated as B–N copolyesters (Figure 1a). These polymers were synthesized by Hoechst-Celanese Corp. The molecular weights were determined by Celanese using inherent viscosity measurements in dilute solution in pentafluorophenol/hexafluoroisopropyl alcohol (PFP/HFIP), and they are listed in Table 1 along with their melting points as determined by DSC at 20 °C/min. The thermal characterization was performed from −50 to +360 °C on annealed samples,[6,7] where the annealing was carried out at temperatures between room temperature and 310 °C. While annealing below 290 °C gave rise to a secondary endotherm, superimposed upon that associated with the mesophase transition, all transitions were completed by 310 °C, the temperature used for the viscosity measurements. It has been reported that these polymers have an exponent close to 1.0 in the Mark–Houwink–Sakurada equation,[8,9] therefore the weight-average molecular weight is about the same as the viscosity-average molecular weight. The nematic–isotropic transition is well above the decomposition temperatures for these materials, which is as high as 450 °C.[7] These copolyesters have an estimated polydispersity of about 2.[8,9] They were dried under vacuum at 120 °C for 24 h prior to testing in order to remove moisture and stored in a desiccator at room temperature until use (the storage time never exceeded 1 week).

We also investigated the aromatic ester oligomer bis[4-(phenoxycarbonyl)phenyl] 1,4-benzenedicarboxylic acid ester (Figure 1 (1)), synthesized as a part of a related project.[10] The sample, after purification by successive recrystallizations in dimethyl sulfoxide (DMSO), was stored in a desiccator at room temperature until use. The solid–nematic transition, as determined by DSC at 20 °C/min, is 251.5 °C, with an enthalpy of fusion of 63.0 J/g. The nematic–isotropic transition could be observed at higher heating rates where degradation was minimum. At 150 °C/min this transition was seen at 392 °C, with an enthalpy of fusion of 4.0 J/g.

For rheological tests the polymers were fabricated into disks, 25 mm in diameter and 1.1 mm in thickness, by hot-pressing at temperatures about the melting point. As-molded fresh samples were loaded in the preheated rheometer, heated up to 310 °C at 30 °C/min, and held for 10 min to allow for thermal equilibrium before measurements started. Measurements were conducted in a nitrogen atmosphere. Experiments were repeated not less than five times (for each sample) to check reproducibility, and in each case a fresh sample was used. Because the material was observed to produce significant outgassing at temperatures above 320 °C, resulting in bubbles forming in the melt,[11] the measurements were made at 310 °C, where the material shows stable rheological properties.[11–14] Thermal stability at 310 °C was tested by oscillatory measurements for a period of 2000 s. Changes in dynamic viscosity of no more than 10% were then taken as the stability criteria.

The rheological characterization was carried out in a Rheometrics Dynamic Spectrometer II (RDS-II) equipped with a

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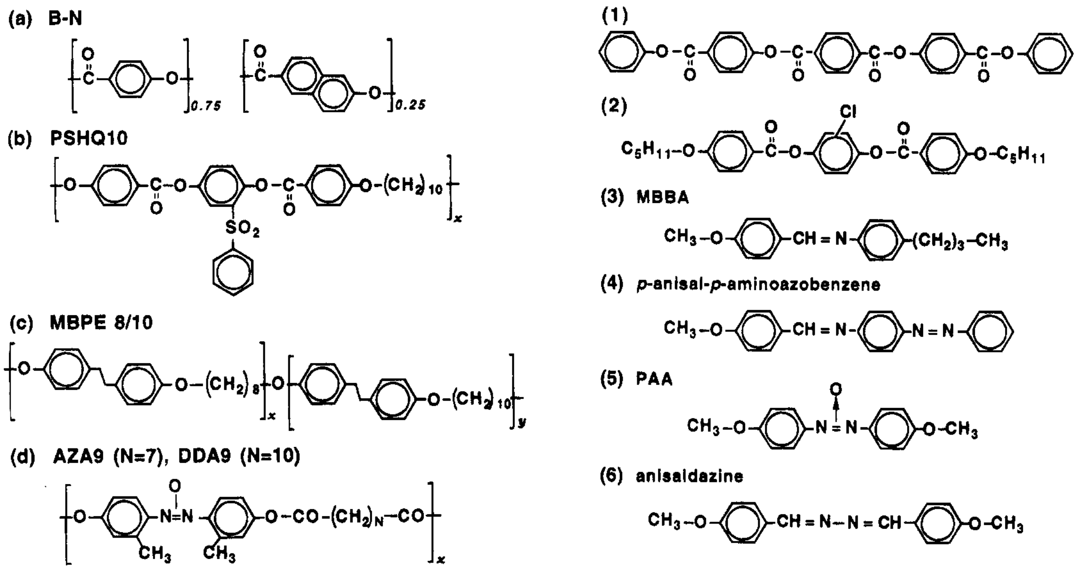

Figure 1. Chemical formula and temperature at which the viscosity was neasured for main-chain thermotropic liquid crystalline polymers (LCPs) and small-molecule liquid crystals (SMLC) plotted in Figure 2. LCPs: (a) B–N 75–25 mol %, 310 °C, this work; (b) PSHQ10, 140 °C, Kim and Han;[18] (c) MBPE 8/10 103 °C, Heberer *et al.*;[19] (d) AZA9 and DDA9, $1.03 \leq T_{red} \leq 1.06$, Blumstein *et al.*[25] SMLCs: (1) bis[4-(phenoxycarbonyl)phenyl] 1,4-benzenedicarboxylic acid ester, 310 °C, this work; (2) 112 °C; (3) MBBA, 25 °C; (4) *p*-anisal-*p*-aminoazobenzene, 160 °C; (5) *p*-azoxyanisole–PAA, 120 °C; (6) anisaldazine, 170 °C.

Table 1. Wholly-Aromatic B–N Copolyesters of 75–25 mol % Composition, with Varying Molecular Weights

M_w[a]	T_m (°C)	M_w[a]	T_m (°C)
4600	272	14400	288
5000	272	30000	295
8600	274		

[a] M_w is the weight-average molecular weight, based on viscosity measurements (Hoechst-Celanese Corp.).

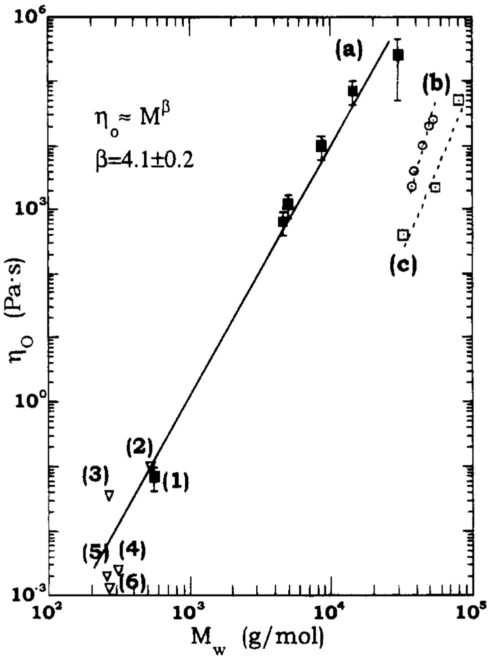

Figure 2. Viscosity data for B–N 75–25 mol % main-chain thermotropic random copolymers, and an aromatic ester oligomer, without flexible spacers, measured in the nematic phase at 310 °C (■). The continuous straight line corresponds to the best fit to our data and has been extrapolated to the lowest data values just as a guide. Data corresponding to SMLCs (▽), taken from the literature,[15] and those reported for Kim and Han[18] (○) and Heberer *et al.*[19] (□), for main-chain thermotropic polymers with flexible spacers in the backbone, are also plotted for comparison. The corresponding chemical formulas are shown in Figure 1.

2000 *g*·cm maximum torque force rebalance transducer and using 25-mm-diameter parallel plates at a constant separation of 1 mm.

Results

Values of the zero-shear viscosity, η_0, were calculated from small-strain oscillatory measurements and are plotted in Figure 2 as a function of molecular weight (■). The viscosity values obtained by this method are in fair agreement with the apparent viscosities obtained from steady-state measurements taken between 0.005 and 10 s^{-1} shear rate. All the copolyesters show a Newtonian plateau at lower shear rates, except in the case of the highest molecular weight available, which is represented by the commercial copolyester Vectra A900. In that case shear-thinning behavior was observed over the full range of shear rates, and this observation is in agreement with Guskey and Winter.[11]

The log–log plot of the data shows that the viscosity dependence of molecular weight can be represented by a straight line of gradient of the order of 4. The exponent obtained for these thermotropic copolyesters and associated oligomer is quite close to, although distinctly different from, the value of 3.4 typical of highly entangled polymeric melts.[15,16] Viscosities for SMLCs are also plotted using values reported in the literature.[17] We observe that they fall fairly close to a linear extrapolation of our polyesters.

The best fit to the experimental data in a log–log plot gives a slope of 4.1 ± 0.2. The uncertainty in the exponent is based on the calculated dispersion of experimental points about the best fit obtained from the least-squares method. The error bars in the plot correspond to the uncertainty in the reproducibility of the experimental values, which never exceeded 20%. No errors have been included for the molecular weight data, as we have used values supplied to us with the polymer series.

Recently, other researchers[18,19] have reported the dependence of rheological properties upon molecular weight for main-chain liquid crystalline polymers with flexible spacers in the backbone. Their results are also plotted in Figure 2 for comparison. Kim and Han[18] measured the zero-shear rate viscosity for the thermotropic aromatic polyesters poly[(phenylsulfonyl)-*p*-phenylene-1,10-decamethylenebis(4-oxybenzoate)] (Figure 1b). They obtained the relationship $\eta_0 \propto M^6$, while corresponding measurements in the isotropic phase gave $\eta_0 \propto M^{6.5}$. Data of Heberer *et al.*[19] for the thermotropic polyethers 1-(4-hydroxyphenyl)-2-(methyl-4-hydroxyphenyl)ethane (Figure 1c) are also plotted in Figure 2. Their results gave a molecular weight exponent in the range 3.5–5, establishing a corresponding relationship in the isotropic phase of $\eta_0 \propto M^4$.

It is also important to note the data of Esnault *et al.*[20] on poly(4,4′-dioxy-2,2′-dimethylazoxybenzenediylnonanediyl) (AZA9; Figure 1d), a thermotropic LCP with flexible spacers in the main chain. These authors established the twist viscosity γ_1 dependence upon molecular weight from NMR measurements. Their data, corrected for order parameter, established a power dependence of 4.7 ± 0.3, *i.e.*, $\gamma_1 \propto \bar{M}_n^{4.7}$.

Our viscosity measurements for liquid crystalline polyesters, covering 8 decades in viscosity, have established that they scale with molecular weight as $\eta_0 \propto M^{4.1}$. This exponent is in the general range of that reported for nematic LCPs with flexible spacers.[18-20]

Discussion

Figure 2 compares the new data for aromatic polyesters (a) with those reported for nematic polymers containing flexible spacers (b and c). The latter data are displaced to lower viscosities for a given molecular weight by about 2 orders of magnitude. We suggest that the effective rod length is shortened by virtue of the flexible links which increase the likelihood of hairpin folds.[21,22] Data from oscillatory measurements on nematic polymers containing flexible spacers (AZA9 and DDA9) due to Blumstein *et al.*[25] are also displaced to lower viscosities but by not as much. They are not plotted because of a question over the precise comparability of their viscosity parameter with ours.

The power dependence of the flexible spacer data is in good agreement with the value of 4.1 for our polymers without flexible spacers (Heberer *et al.*[19] $\beta = 3.5 \rightarrow 5$; Blumstein *et al.*,[25] $\beta = 3.95$), with the exception of that of Kim and Han,[18] who quote $\beta = 6$ from their data. The somewhat high power dependences reported for the flexible spacer materials (6 and $3.5 \rightarrow 5$)[18,19] are closer to the case of rodlike macromolecules in the isotropic case predicted by Doi and Edwards,[23] where $\eta_0 \propto M^6$, than that obtained for the all-aromatic LCPs. However, those data were obtained in smaller ranges of molecular weight than in the current study, and thus the value of the exponent may be subject to greater uncertainty.

Klein *et al.*[24] (from the same laboratory as ref 20) measured the rotational viscosity of poly[oxy(3-methyl-1,4-phenylene)oxy(1,12-dioxo-1,12-dodecanediyl)] (DDA9; similar to AZA9 polymer but differing by the number 10 instead of 7 and parity of methylene groups in the spacer), with NMR giving an exponent of 6.0. In explaining these values (4.7[20] and 6.0[24]) Esnault *et al.*[26] drew a distinction between "large" viscosities γ_1, γ_2, α_1, α_2, η_c and "small" viscosities α_3, η_b, η_{bend}, with the latter group having values 1–2 orders of magnitude less than the former for polymers, although having similar values for small molecules. We suggest that, as suggested by rheo-optical experiments,[27] at high shear rates the director is aligned with the shear direction. Consequently, the values of the viscosity coefficient measured under shear in the nematic phase and extrapolated to zero-shear rate are expected to be close to η_b, the second Miezowicz coefficient[3] and one of the "small" coefficients at high molecular weights.

We conclude that the dependence of viscosity on molecular weight for nematic copolyesters without flexible spacers is 4.1. This value is distinctly different from that of conventional polymer melts, 3.4, but lies within the range of values reported for nematic polymers with flexible spacers.

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References and Notes

(1) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, U.K., 1992.
(2) Ciferri, A. *Liquid Crystallinity in Polymers: Principles and Fundamental Properties*; VCH Publishers: New York, 1991.
(3) de Gennes, P.-G. *The Physics of Liquid Crystal*; Clarendon Press: Oxford, U.K., 1974.
(4) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1986.
(5) The molten phase of the B–N random copolyesters is considered here to be nematic, although it has been proved that this mesophase contains segregated sequences of mesogenic units, forming smectic-type regions: Hanna, S.; Romo-Uribe, A.; Windle, A. H. *Nature* **1993**, *366*, 546.
(6) Lemmon, T. Ph.D. Thesis, University of Cambridge, Cambridge, U.K., 1989.
(7) Anwer, A. Ph.D. Dissertation, University of Cambridge, Cambridge, U.K., 1990.
(8) Calunndan, G. W.; Jaffe, M. The Robert A. Welch foundation conferences on chemical research, XXVI. Synthetic polymers, Houston, TX, Nov 15–17, 1982.
(9) Krömer, H.; Khun, R.; Pielartzik, H.; Siebke, W.; Eckhardt, V.; Schmidt, M. *Macromolecules* **1991**, *24*, 1950.
(10) Mooney, J. A. Ph.D. Thesis, University of Cambridge, Cambridge, U.K., 1990.
(11) Guskey, S. M.; Winter, H. H. *J. Rheol.* **1991**, *35*, 1191.
(12) Lin, Y. G.; Winter, H. H. *Macromolecules* **1988**, *21*, 2439.
(13) Lin, Y. G.; Winter, H. H. *Macromolecules* **1991**, *24*, 2877.
(14) Cochinni, F.; Nobile, M. R.; Acierno, D. *J. Rheol.* **1991**, *35*, 1171.
(15) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(16) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(17) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag-Chemie: Weinheim, Germany, 1980.
(18) Kim, S. S.; Han, C. D. *Macromolecules* **1993**, *26*, 6633.
(19) Heberer, D. P.; Odell, J. A.; Percec, V. *J. Mater. Sci.* **1994**, *29*, 3477.
(20) Esnault, P.; Volino, F.; Martins, A. F.; Kumar, S.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 143.
(21) Kent, S. L.; Geil, P. H. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *B30*, 1489.
(22) Irwin, R. S. *Macromolecules* **1993**, *26*, 7125.
(23) (a) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 560. (b) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 918.
(24) Klein, T.; Jun, H. X.; Esnault, P.; Blumstein, A.; Volino, F. *Macromolecules* **1989**, *22*, 3731.
(25) Blumstein, A.; Thomas, O.; Kumar, S. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 27.
(26) Esnault, P.; Casquilho, J. P.; Volino, F.; Martins, A. F.; Blumstein, A. *Liq. Cryst.* **1990**, *7*, 607.
(27) Alderman, N. J.; Mackley, M. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 149.

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